UNIVERSITI PUTRA MALAYSIA

PREPARATION OF POLY(STYRENE) GRAFTED OIL PALM EMPTY FRUIT BUNCH FIBER AND ITS APPLICATION AS A FILLER FOR HIGH IMPACT POLY(STYRENE) COMPOSITES

JAMAROSLIZA JAMALUDDIN.

PREPARATION OF POLY(STYRENE) GRAFTED OIL PALM EMPTY FRUIT BUNCH FIBER AND ITS APPLICATION AS A FILLER FOR HIGH IMPACT POLY(STYRENE) COMPOSITES

By

JAMAROSLIZA BINTI JAMALUDDIN

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirement for the Degree of Master of Science

December 2005

Khas untuk Abah & Mak

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Master of Science

PREPARATION OF POLY(STYRENE) GRAFTED OIL PALM EMPTY FRUIT BUNCH (OPEFB) FIBER AND ITS APPLICATION AS A FILLER FOR HIGH IMPACT POLYSTYRENE (HIPS) COMPOSITES

By

JAMAROSLIZA BINTI JAMALUDDIN

December 2005

Chairman : Professor Wan Md Zin Wan Yunus, PhD

Faculty : Science

Polystyrene (PS) was grafted onto oil palm empty fruit bunch (OPEFB) fiber in aqueous medium using H_2O_2/Fe^{2+} initiator system. The grafting percentage was found to be dependent on the reaction period and temperature, amounts of the monomer, the initiator and the cocatalyst. The maximum percentage of grafting (of about 200%) was achieved when the reaction was carried out under the following conditions: reaction period; 4 hours, reaction temperature; 65°C, amounts of monomer; 52.27 mmol, amounts of initiator; 6.00 mmol and amounts of cocatalyst; 0.26 mmol. The reaction mechanism for the grafting of styrene onto OPEFB fiber was proposed and proof of grafting was confirmed by scanning electron microscopy (SEM) and Fourier-transform infrared (FT-IR) analysis. The presence of a peak around 3026 cm^{-1} and two peaks between 698 and 755 cm^{-1}in the FTIR of the product provides strong evidence on the presence of poly(styrene) in the product. The effects of grafting on the thermal

properties were studied by thermogravimetry analysis (TGA). Preparation of composite samples were carried out by melt blending in Haake plasticorder with rotor speed of 40 rpm at 170°C for 10 minutes, and then followed by hot pressing moulding. The tensile properties of high impact polystyrene (HIPS) reinforced with OPEFB, OPEFB-g-PS and crude OPEFB-g-PS fiber were studied. By using OPEFB-g-PS and crude OPEFB-g-PS as the filler, it was found that the tensile property of the resulting composites was enhanced. The tensile strength of OPEFB-g-PS and crude OPEFB-g-PS/HIPS composites shows marginal increase up to 20% of filler content but decreases with further increase of the filler content. The incorporation of OPEFB fiber considerably improves the young modulus of the composite but is more significant when using OPEFB-g-PS and crude OPEFB-g-PS as the filler in HIPS composite. The elongation at break decreases with the increase of the filler content. The SEM micrograph shows that the interfacial adhesion between the OPEFB-g-PS and crude OPEFB-g-PS fibers with HIPS matrix are considerably improved compared to that of OPEFB fiber-HIPS composites. The water absorption of the composites increases as the filler loading is increased. However, by grafting poly(styrene) onto OPEFB fiber, the hygroscopicity of the composites can be reduced. The thermal stability of OPEFB-g-PS/HIPS and crude OPEFB-g-PS/HIPS composites are improved. Fourier transform infrared (FTIR) spectroscopy shows that the hydroxyl group absorption shift to lower wave numbers which indicates that the hydrogen bonding is formed. The study of the effect of adding various amount of the OPEFB-g-PS fiber into OPEFB/HIPS (20:80) composites was also carried out. Incorporation of the OPEFB-g-PS in these composites also improves the tensile strength and young modulus.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENYEDIAAN POLISTIRENA DICANGKUKKAN KE ATAS GENTIAN TANDAN KELAPA SAWIT (OPEFB) DAN APLIKASINYA SEBAGAI PENGISI BAGI KOMPOSIT POLISTIRENA HENTAMAN TINGGI (HIPS)

Oleh

JAMAROSLIZA BINTI JAMALUDDIN

Disember 2005

Pengerusi : Profesor Wan Md Zin Wan Yunus, PhD

Fakulti : Sains

Polistirena (PS) dicangkukkan ke atas gentian tandan kelapa sawit (OPEFB) dalam medium berair menggunakan sistem mangkin H_2O_2/Fe^{2+}. Peratus cangkukan didapati bergantung kepada masa tindakbalas dan suhu, kuantiti monomer, mangkin dan ko-mangkin. Peratus maksimum cangkukan (lebih kurang 200%) dicapai apabila tindakbalas dijalankan di bawah keadaan: masa tindakbalas; 4 jam, suhu tindakbalas; 65°C, kuantiti monomer; 52.27 mmol, kuantiti mangkin; 6.00 mmol dan kuantiti ko-mangkin; 0.26 mmol. Mekanisma tindakbalas untuk cangkukan stirena ke atas gentian OPEFB dicadangkan dan bukti cangkukan disahkan dengan mikroskopi pengimbas elektron (SEM) dan analisis Inframerah Fourier (FTIR). Kehadiran puncak sekitar 3026 cm^{-1} dan dua pucak di antara 698 dan 755 cm^{-1} di dalam FTIR menunjukkan bukti yang kuat kehadiran PS dalam produk. Kesan cangkukan ke atas sifat terma dijalankan menggunakan analisis termogravimetri (TGA). Penyediaan sampel komposit dilakukan

secara pengadunan leburan di dalam Haake Plasticorder dengan kelajuan rotor 40 rpm pada 170°C selama 10 minit, diikuti dengan pengacuan mampatan panas. Sifat tensil bagi polistirena hentaman tinggi (HIPS) yang diperkuatkan dengan OPEFB, OPEFB-g-polistirena dan 'crude' OPEFB-g-polistirena dikaji. Dengan menggunakan OPEFB-g-polistirena dan 'crude' OPEFB-g-polistirena sebagai pengisi di dapati meningkatkan sifat tensil bagi komposit tersebut. Kekuatan tensil bagi OPEFB-g-polistirena dan 'crude'OPEFB-g-polistirena/HIPS komposit menunjukan peningkatan yang kecil sehingga pembebanan pengisi 20% tetapi menurun apabila pembebanan pengisi bertambah. Modulus young bagi komposit meningkat dengan kehadiran gentian OPEFB tetapi peningkatan lebih ketara apabila menggunakan OPEFB-g-polistirena dan 'crude' OPEFB-g-polistirena sebagai pengisi di dalam komposit HIPS. Pemanjangan pada takat putus menurun apabila pembebanan pengisi bertambah. Mikrograf SEM menunjukkan perlekatan antarafasa di antara OPEFB-g-polistirena dan 'crude' OPEFB-g-polistirena dengan matrik HIPS adalah lebih baik dibandingkan dengan komposit OPEFB/HIPS. Kadar penyerapan air bertambah apabila pembebanan pengisi bertambah. Walaubagaimanapun dengan mencangkukkan polistirena ke atas gentian OPEFB boleh mengurangkan higroskopik komposit tersebut. Kestabilan terma bagi komposit OPEFB-g-PS/HIPS dan 'crude' OPEFB-g-PS adalah lebih baik. Analisis sinaran inframerah fourier (FTIR) menunjukan penyerapan kumpulan hidroksil beralih ke nombor gelombang yang lebih rendah. Ini bermakna terbentuknya ikatan hidrogen. Kajian terhadap kesan penambahan pelbagai kuantiti OPEFB-g-polistirena kedalam komposit OPEFB/HIPS (20:80) juga dijalankan. Penambahan OPEFB-g-polistirena di dalam komposit ini juga meningkatkan kekuatan tensil dan modulus young.

ACKNOWLEDGEMENTS

First and foremost I would like to extend my heartiest thanks to my supervisor, Professor Dr. Wan Md Zin Wan Yunus for his guidance, constructive comments, continuous support and advice throughout the duration of my study. I am indebted to his faith in me which motivated me to proceed and persist. To the rest of my committee, Associate Professor Dr. Mansor Bin Ahmad and Associate Professor Dr. Mohamad Zaki Ab. Rahman, I would like to express my appreciation for their advice and support. Additionally, I would like to express my gratitude and compliments to Puan Norazowa for her invaluable guidance, continuous encouragement and support.

A warm thanks is extended to Dr Fauziah for allowing me to use the equipment in Bioscience Institute. Also thank you to all the staff in Electron Microscopy unit, Bioscience institute especially Puan Azila and En Safarin. Sincere thanks also extended to all laboratory assistants in the Chemistry Department, UPM for their assistance. Thanks also go out to my friends Aidil, Guna, Wei Chee, Sharil, Sharifah, Abby, Zuliyana and Zulhisham. Each of them has helped me in their own way.

Also, I must give credit to my parents for their deepest love, encouragement and motivation which always seemed to be given at just the right moment. I wish to extend a heartfelt appreciation to all my family members and my fiancée, Nazri who have had utmost confidence in my endeavor. Special thanks to Universiti Teknologi Malaysia for their financial support and study leave.

I certify that an Examination Committee has met on 27 December 2005 to conduct the final examination of Jamarosliza Binti Jamaluddin on her Master of Science thesis entitled "Preparation of Poly(styrene) Grafted Oil Palm Empty Fruit Bunch Fiber and its Application as a Filler for High Impact Poly(styrene) Composites" in accordance with Universiti Pertanian (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

Mohd Zobir Hussein, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Md.Jelas Haron, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Imad (Moh'd Khair) Rashid Hamadneh, PhD
Lecturer
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Khairul Zaman Hj. Mohd. Dahlan, PhD
Malaysian Institute for Nuclear Technology Research
(External Examiner)

HASANAH MOHD GHAZALI, PhD
Professor/Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

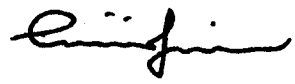
Date: 15 JUN 2006

This thesis submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee are as follows:

Wan Md. Zin bin Wan Yunus, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Mansor bin Ahmad, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Mohammad Zaki Abdul Rahman, PhD
Associate Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

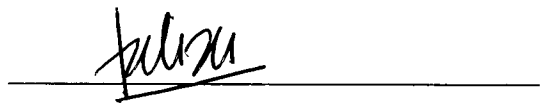


AINI IDERIS, PhD
Professor/Dean
School of Graduate Studies
Universiti Putra Malaysia

Date: 13 JUL 2006

DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.



JAMAROSLIZA BINTI JAMALUDDIN

Date: 16/5/06

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

AA	Acrylamide
AN	Acrylonitrile
ASTM	American society for testing materials
BA	Butyl acrylate
CAN	Ceric ammonium nitrate
Crude OPEFB-g-PS	OPEFB grafted polystyrene with homopolymer
DTG	Differential thermogravimetric
$CuSO_4$	Copper sulphate
E_b	Elongation at break
FTIR	Fourier transform infrared
HDPE	High density polyethylene
HIPS	High impact polystyrene
H_2O_2	Hydrogen peroxide
MAPP	Maleic anhydride-grafted polypropylene
MMA	Methyl methacrylate
$NaIO_4$	Sodium periodate
NaOH	Natrium hidroksida
OPEFB	Oil palm empty fruit bunch
OPEFB-g-PS	OPEFB grafted polystyrene
OPWF	Oil palm wood flour
PBS	Poly(butylenes succinate)

PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl chloride
SEM	Scanning electron microscopy
TGA	Thermogravimetry analysis
$T_{5\%}$	The onset temperature of a 5% weight loss deviation from base line
wt %	Weight percent

CHAPTER 1

INTRODUCTION

1.1 Introduction

In recent years, significant efforts have been made to manufacture natural fibers reinforced thermoplastic composites. The rationale behind these efforts is that the use of natural fibers offers several advantages, such as low cost, low density, high toughness, acceptable specific strength, enhanced energy recovery, recyclables and biodegradability (Misra *et al.* 2003).

Lignocellulosic filler and fiber have recently been investigated in synthetic polymer composite systems. Their potential to enhance the mechanical properties over a neat polymer matrix (particularly impact toughness and stiffness) and to reduce the final cost of the material as well as to increase the biodegradable component content within the materials make the use of biobased polymer very attractive. Cellulose-containing fibers such as wood fiber, sisal fiber and rice straws have been studied in the context of their reinforcing properties within conventional thermoplastic materials. Various matrix materials combine with natural fibers including polypropylene (Ichazo *et al.* 2000), various polystyrene (Maldas *et al.* 1988; Nair *et al.* 1996; Maldas *et al.* 1989), polyethylene (Raj *et al.* 1989) and polyvinyl chloride (Kamel, 2004).

A common problem associated with these composite systems is poor interfacial adhesion between the hydrophobic matrix material and the hydrophilic filler, which contributed to the poor mechanical properties in the final material. This problem may be addressed by grafting hydrophobic vinyl monomer onto backbone of cellulose fiber.

Grafting of synthetic polymeric chains is one of the most recurrent used methods to increase the compatibility between cellulose and a variety of synthetic polymer (Bledzki and Gassan, 1999). Grafting of lignocellulosic material such as sisal fiber (Mishra *et al.* 2001), jute (Chauhan *et al.* 2000; Mohanty and Singh, 1998; Gosh and Ganguly, 1994; Moharana and Tripathy, 1991), kenaf (Eromosele and Bayero, 1999) and pineapple leaf (Mohanty *et al.* 1996) have been done successfully using a different type of initiator.

In this research oil palm empty fruit bunch (OPEFB) are grafted with polystyrene to modify the surface of OPEFB from hydrophilic to hydrophobic fillers and make it compatible with hydrophobic matrices when it is used as filler in high impact polystyrene (HIPS) composite.

OPEFB fiber is a natural fiber derived from an oil palm tree (*Elaeis guineesis*). It is one of the lignocellulosic materials of great importance in Malaysia since a large quantity is generated by oil palm industries, which is estimated to be about 8 million tones peryear (Rozman *et al.* 2000). The utilization of OPEFB offers several advantages such as low density, greater deformability, less abrasiveness to equipment, biodegradability, cheap

and also reduces environmental problems related to the disposal of the oil palm wastes (Rozman *et al.* 2001).

1.2 Copolymers

A polymer whose chain molecules are composed of more than one kind of repeating chemical units is commonly called copolymer (Ghosh, 2002). The copolymer is categorized into four types depending on the orders of monomer in the polymer backbone.

1. Alternating copolymers: When the monomers are arranged in alternating fashion. The alternating copolymer is represented as follows:

$$-A-B-A-B-A-B-A-B-A-B-A-B-A-B-$$

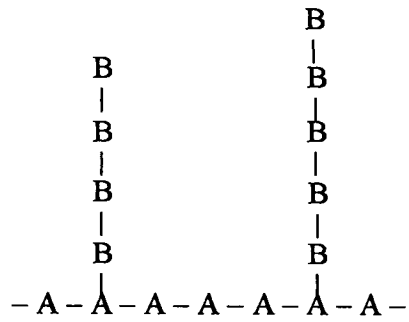
2. In a random copolymers, the monomers may follow in any order:

$$-A-A-B-A-B-B-A-A-B-B-B-A-B-B-$$

3. Block copolymers are polymer chains consisting of segments with different chemical composition. The block copolymers is represented as follows:

$$-A-A-A-A-A-A-A-B-B-B-B-B-B-B-$$

4. Graft copolymers: Graft copolymers are prepared when long or short sequences of one monomer appear as grafted or pendent chains linked to a backbone of long sequences of another monomer. The structure is assumed as follows:



(Note: A and B are different monomer units)

1.3 Thermoplastics

Thermoplastics offer many advantages over traditional materials such as low density, low energy for manufacturing and low processing costs. Thermoplastic also can be reshaped and recycled (Crawford, 1981). It's generally divided into two classes of molecular arrangement, amorphous and semicrystalline. Amorphous and semicrystalline structures are showed in Figures 1.1(a) and 1.1(b) respectively.

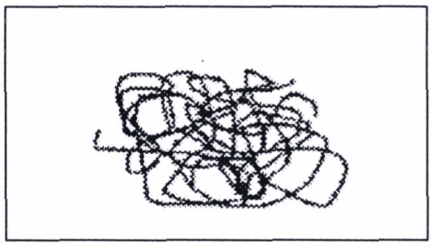


Figure 1.1(a): Amorphous

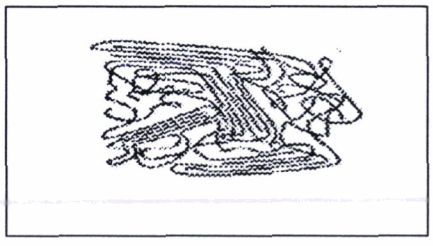


Figure 1.1(b): Semicrystalline

1.4 Polymer-Fiber Composites

A polymer-fiber composite is any material made of a fiber and a matrix (Figure 1.2).

The matrix, which is a stuff that holds the fibers, transfers applied load to these fibers and protect them from harmful environmental effects. When the composite material is formed into a shape, the matrix protects the fiber from damage. Thermosets and thermoplastic are an examples of ideal matrices (Jayaraman, 2003).